Theor Chem Acc (2001) 105:276–283
DOI 10.1007/s002140000233

Theoretical
Chemistry Accounts

Regular article

The zero-flux surface and the topological and quantum definitions of an atom in a molecule

Richard F. W. Bader

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Received: 17 June 2000 / Accepted: 2 October 2000 / Published online: 19 January 2001

Abstract. The partitioning of a charge distribution by surfaces exhibiting a local zero flux in the gradient vector field of the electron density leads to an exhaustive and disjoint division of the system into a set of mono-nuclear regions or atoms, provided the only local attractors present in the system are isolated nuclear attractors and the electronic energy is less than that required to produce the plasma state. The existence of non-isolated attractors, whose limited occurrence is confined primarily to excited state charge distributions of one-electron systems, is shown to be readily encompassed within the topological theory of molecular structure, a theory whose purpose is to relate a system's properties to the observed topology of its density distribution. The zero-flux surface serves as the *necessary* boundary condition for the application of Schwinger's principle of stationary action to define the physics of an atom in a molecule as an open system. Schwinger's principle requires the use of a special class of trial functions: those whose variation is to be equated to the action of smooth, continuous changes in the coordinates of the physical system caused by the action of generators of infinitesimal transformations, the very requirement needed to ensure the applicability of the zero-flux surface condition as the defining constraint of an open system.

Key words: Atoms in molecules – Zero-flux surface – Topological atom

The zero-flux surface

The quantum theory of atoms in molecules [1] is widely employed in the study of the experimentally measured and theoretically determined properties of molecules and crystals, as exemplified in a recent review by Spackman describing its application to the analysis of charge densities obtained from X-ray studies [2]. Within this theory, an atom is defined as a open system, one that is bounded by a surface $S(\mathbf{r}_s)$ of local zero flux in the gradient vector field of the electron density $\rho(\mathbf{r})$, as given in Eq. (1):

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \qquad \forall\ \mathbf{r}\ \in S(\mathbf{r}_s) \tag{1}$$

where $\mathbf{n}(\mathbf{r})$ is a unit vector normal to the surface at $\mathbf{r}$. At the meeting on 'Chemical Bonding' in La Colle-sur-Loup France, my talk emphasized that the adoption of the quantum theory of atoms in molecules requires the replacement of the model of structure that imparts an existence to a *bond* separate from the atoms it links – the ball and stick model or its orbital equivalents of atomic and overlap contributions – with the concept of *bonding* between atoms; two atoms are bonded if they share an interatomic surface and are thus linked by a bond path. It was emphasized that the quantum mechanics of a proper open system not only enables one to define the properties of atoms that are bonded to one another thereby assessing their degree of interaction, but provides, in addition, a characterization of the interaction through the theorems that govern the local behavior of the electron density [3].

This paper takes the opportunity to review and to consider in more detail the topological and mathematical implications of the zero-flux surface and its role in establishing the quantum mechanics of an open system, a move prompted in part in response to questions raised at the meeting.

Point attractors

The density exhibits a local maximum at the position of a nucleus, and a nucleus is an isolated, three-dimensional point attractor that serves as the terminus of the gradient paths in its vicinity. It behaves as does a critical point (CP) of rank three and signature minus three, a (3,−3) CP. While non-isolated attractors of rank one or two, corresponding to global and ring attractors, respectively, defined and described below, are topologically possible, only isolated point attractors of dimensions three, two,

Contribution to the Proceedings of the 2000 Symposium on Chemical Bonding: State of the Art in Conceptual Quantum Chemistry

and one, have so far been observed in experimentally determined charge distributions. Correspondingly, only such isolated point attractors have been theoretically predicted to occur in the electron density distributions of the ground and, with a single exception, excited states of many-electron systems. Indeed, the overwhelming prevalence and ubiquitous occurrence of point attractors in electron density distributions, both predicted and observed, accounts for the success of the atomic concept in the classification and prediction of the observations of chemistry [1, 4] leading one to the immediate realization that the application of Eq (1) to a charge distribution accompanied with the stipulation that the nuclei be excluded from $S(\mathbf{r}_s)$, (along with non-nuclear maxima whose sporadic appearance is discussed below) leads to a disjoint and exhaustive partitioning of space into a set of mononuclear, that is, atomic regions. Fig. 1 illustrates this partitioning of the electron density for a highly excited Rydberg state of the formaldehyde molecule,

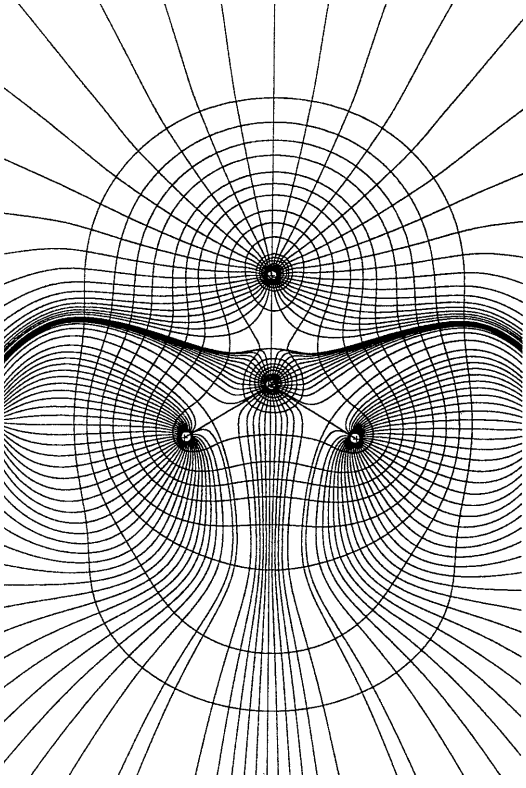

Fig. 1. Contour map of the electron density of the formaldehyde molecule, H_2CO, in the plane of the nuclei for the $2\ ^1B_2$ excited state corresponding to the vertical excitation of an in-plane nonbonded electron on oxygen into a p_σ-like orbital. The Rydberg-like nature of the excitation is evident in the diffuse nature of the outer density, resulting in a 46% increase in the molecular volume enclosed by the outer contour of 0.001 au. The plot is overlaid with trajectories representing the gradient vector field of the electron density. The topology determined by this field is homeomorphic with that exhibited by the ground state charge distribution: each nucleus acts as a point attractor and defines an associated atomic basin with the basins of neighboring atoms being separated by zero-flux surfaces and their nuclei linked by bond paths. The outermost contour value is 0.001 au and the remaining contours increase in value in the order 2×10^n, 4×10^n. 8×10^n au with n beginning at −3 and increasing in steps of unity

demonstrating that the nuclei continue to define their individual domains even in the presence of the diffuse density distribution found in excited states [5]. This partitioning assigns to the nuclei their natural roles as attractors, each dominating its own atomic basin, the region of space traversed by the gradient paths of the density that terminate at, that is, *are attracted to*, that particular nucleus. *An atom is defined as the union of an attractor and its basin.*

The cusp condition

Without the stipulation that the nuclei be excluded from the partitioning surfaces $S(\mathbf{r}_s)$, there are an infinite number of surfaces that would appear to satisfy the zero-flux boundary condition stated in Eq. (1). For example, any region bounded by a set of gradient paths originating at a nucleus and terminating at say a cage critical point, or a set originating at a nucleus and terminating at infinity. However, only by excluding nuclei from the defining surface does one obtain a chemically meaningful partitioning of configuration space, that is, a partitioning into atoms. It is this procedure that yields a unique definition of an atom, as the union of an attractor and its basin. The manifold physical consequences of this definition of an atom, which is a manifestation of the dominance of the nuclear-electron force in determining the form of matter, stand alone as a reason for imposing Eq. (1) with the exclusion of nuclei, as the boundary condition for the definition of an atom, one that applies whether the atom be free or bound.

Nonetheless, because of the nuclear cusp condition, the electron density $\rho(\mathbf{r})$ does not satisfy Eq. (1) at a nuclear position and thus one can make the argument that nuclei are automatically excluded from any zero-flux surface. The statement that the zero-flux condition yields a disjoint and exhaustive partitioning of a system into atomic domains then requires as its sole restrictive condition that only isolated point attractors be present. The cusp condition is clearly an important point, one that merits further discussion in addition to that originally [6, 7] and subsequently given [1].

The Coulombic Hamiltonian, one which treats the nuclei and electrons as point charges, becomes infinite in magnitude whenever two point charges coalesce. As a consequence, Kato [8] demonstrated that the wave function ψ must exhibit cusps – its first derivative becoming discontinuous – when the coordinates of two particles coalesce. In particular, this means that $\nabla\psi$ and hence $\nabla\rho$, the latter as discussed by Steiner [9], are undefined at a nuclear position coordinate. Because of this discontinuous behavior of the gradient of the density at a nuclear position, such coordinates do not satisfy the zero-flux surface condition, Eq. (1), and must be excluded from such surfaces. Thus, for a system of point attractors the atomic partitioning defined by Eq. (1) is unique and exhaustive.

Now, of course, nuclei are not point charges, exhibiting a radius R proportional to their mass number A, with $R = 1.4\ A^{1/3} \times 10^{-13}$ cm [10]. So the question must be asked as to whether the finite size of a nucleus in-

validates the use of the Coulombic Hamiltonian in the application of quantum mechanics to chemistry, and in particular to the study of the topological properties of the electron density. One should recall that every Hamiltonian that one uses to describe a given system and predict its properties is a model Hamiltonian. One chooses a Hamiltonian on the basis of its ability to recover the known or measured physics of the system under study. We are fortunate in this regard with respect to the question of the suitability of the Coulombic Hamiltonian, in that this question has been unequivocally answered experimentally through the study of the scattering by nuclei of high energy electrons. For high enough energies, the de Broglie wave length of the electron becomes comparable to the nuclear radius R and the scattering of high energy electrons can be used to gain information about the charge distribution within a nucleus. Elton [11] has considered the elastic scattering of high energy electrons from nuclei using both the Coulomb potential for a point nucleus and potentials that model the effects of a nucleus of finite size. He finds that for energies up to 40 MeV for light nuclei and for energies less than 20 MeV for heavy nuclei, no errors are introduced into the calculated scattering intensities through the use of the nuclear point charge model. (The de Broglie wave length of a 20 MeV electron equals 3×10^{-11} cm, approximately one hundred times larger than the radius of a nucleus of mass number 200.) From an operational point of view, the potential exerted by the nucleus on an electron is sensibly Coulombic, even for energies well beyond any encountered in chemistry. One readily calculates that the energy required to ionize the remaining electron from a U^{+91} ion is only 0.12 MeV, well below that required to cause the electron to view the nucleus as other than a point attractor. Thus, the Coulombic Hamiltonian will introduce no errors for any system possessing energies short of those required to generate a plasma. It is also important to note that the relativistic solutions for a hydrogen-like atom contain the factor e^{-ar} and hence both radial components to the spinor exhibit cusps [12]. Thus, extending the Hamiltonian to include relativistic effects when v/c approaches unity will not affect the cusp condition. In addition, since the two components of the spinor are differently affected, the nodes in the excited state solutions vanish with the inclusion of relativistic effects. One concludes that *the use of the cusp condition in the definition of an atom is completely acceptable up to energies that would result in the formation of a plasma and for a Hamiltonian that includes relativistic effects*.

Because of the cusp condition, the local maxima exhibited by the density at the nuclear positions are not true critical points. However, as previously pointed out, there always exists a function homeomorphic to the density which coincides with it almost everywhere and for which the nuclear positions are (3,−3) critical points. In this sense, the nuclear positions behave topologically as do (3,−3) critical points in the charge density. It is worthwhile noting that this interpretation is consistent with the observed satisfaction of the Poincaré-Hopf relationship that governs the number of rank three critical points of each type that can co-exist for a given finite number of point attractors when identified at (3,−3) critical points, as found in isolated molecules [1] or for an infinite lattice of attractors, as found in a crystal [13, 14]. The satisfaction of the Poincaré-Hopf relationship for molecules or the related Morse relations [14] demonstrates that operationally, the homeomorphic identification of the nuclear maxima in the density with (3,−3) critical points is topologically correct.

The periodicity present in a crystal prompted Pendás et al. [14] to introduce the concept of a primary bundle, the set of trajectories of $\nabla\rho(\mathbf{r})$ with common α and ω limits; the bundle of trajectories starting at a cage CP and terminating at a nuclear maximum, for example. The union of all primary bundles sharing a common nuclear attractor or maximum provides an alternative definition of an atomic or attractor basin, one which suggests the symmetrical definition of a repulsion basin as one generated by all of the bundles sharing a common cage CP, or density minimum in its interior. The two basins provide complementary views of a crystal structure: an attractor basin is a polyhedron with as many faces as there are bonded neighbors, while a repulsion polyhedron has vertices along the bond paths. Pendás et al. state that the boundary surface of a primary bundle is a zero-flux surface, which it is for every point on the surface with the exception of the nuclear position.

The existence of non-nuclear maxima in the density, that is, non-nuclear attractors, is now well established, both experimentally and theoretically. The value of $\rho(\mathbf{r})$ at the maximum is small and only slightly in excess of the values at its connecting (3,−1) CPs. In addition, the curvatures of the density at the maximum are of small magnitude. This behavior is typified by the non-nuclear maximum that is found to characterize an F-center in an alkali halide crystal, where $\rho(\mathbf{r}_c) = 0.018$ au and $|\nabla^2\rho(\mathbf{r}_c)| = 0.015$ au [15]. A non-nuclear maximum in the density is a (3,−3) CP and while any bundle of gradient paths terminating at the CP will be bounded by a zero-flux surface, there is no physical basis for associating other than the basin defined by the complete set of trajectories that terminate at the CP with its presence, a procedure that results in the exhaustive partitioning of the space of the crystal or molecule containing such CPs into regions, each of which contains a point attractor. In the identification of an F-center in an alkali halide crystal with the basin of a non-nuclear maximum for example, one determines it to have a population of 0.63 e and an energy of −3.5 eV, compared to the calculated energy of 4.9 eV required for the ionization of the odd electron.

Ring and global attractors

The existence of non-isolated maxima in $\rho(\mathbf{r})$ as found in the excited states of one-electron systems for example, was previously recognized [1, 16]. Since there is little chemical literature devoted to such systems, they did not seem to justify any fuller discussion at the time the theory was under development. Nonetheless, the identification of the critical points in $\rho(\mathbf{r})$ and their association with chemical concepts is readily extended to the density

distributions exhibited by such excited states through the recognition of *global* and *ring* attractors, in addition to the ubiquitous isolated *point* attractors and, in so doing, one completes the description of the possible attractors that can be identified in the charge density or any three-dimensional scalar field.

The nodal surface in the 2S excited state of the hydrogen atom is a zero-flux surface that satisfies Eq. (1). Its presence is used to exemplify the definition and properties of a global attractor. Global attractors are not new to the topological study of the density, being present in the Laplacian of the electron density of the ground states of many-electron atoms [1]. The density of the 2^2S state of hydrogen exhibits a local maximum at the nucleus and a surface of radius 5 au over which $\rho(\mathbf{r})$ attains its maximum radial value, with an intervening nodal surface of radius 2 au. Topologically, a zero-flux surface (aside from the one at infinity) always represents a partitioning between attractor domains. Thus, the surface over which $\rho(\mathbf{r})$ attains its maximum value in the 2S state is a surface of critical points, that is, non-isolated, degenerate critical points, each of rank 1 and signature -1, a $(1,-1)$ critical point (CP) which shall be termed a 'global' attractor. The axis of the single non-vanishing negative curvature at each CP is directed along a radial coordinate, the curvatures associated with the two axes tangent to the sphere of maximum density necessarily equaling zero. The spherical surface over which $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ attains its maximum value within a shell of charge concentration in the Laplacian distribution, is also a global attractor. All the points of the global attractor in the 2S state are linked to the nuclear point attractor by an infinite number of pairs of trajectories which originate in the zero-flux surface, a surface composed of $(1,+1)$ CPs; one trajectory of each pair terminates at the nucleus, the other at the radially directed point (a radial maximum) in the global attractor. Thus, the nucleus is linked by a bond path to each point of the global attractor, the $(1,+1)$ CP being the global analogue of a $(3,-1)$ CP. All of the ideas associated with point attractors survive for the global attractor, with the nuclear attractor linked by a bond path to every global point attractor and with the basin of the point and global attractors separated by a zero-flux surface. The difference being that in an excited S state one 'attractor' consists of a global set, an infinite number of attractors all of rank one forming a spherical surface.

An excited Π state of Li_2^+, which behaves as an effective one-electron system, does not exhibit the usual single $(3,-1)$ CP between at the mid-point of the internuclear axis, but instead a torus of non-isolated degenerate (2,0) CPs encircling the mid-point, that is, a ring of maximum density encircling the axis [16]. The negative curvature at each point on the (2,0) ring attractor defines a pair of trajectories one of which is directed and terminates at a $(3,+3)$ or cage CP, a local minimum in $\rho(\mathbf{r})$ located at the mid-point of the axis. The positive curvature defines a unique pair of trajectories each of which terminates at one of the nuclei, a bond path linking each point in the ring attractor to the nuclei. In this instance of a ring attractor, the nuclei are linked by two cones of bond paths. Analogous ring attractors are found in $L(\mathbf{r})$ distributions, the associated bond paths linking the bonded charge concentrations lying within the basins of the neighboring atoms, as found in N_2 or F_2, for example [17]. Thus, attractor domains can be linked by a single bond path originating from an isolated $(3,-1)$ CP, by two cones of bond paths generated by a torus of (2,0) CPs or by an infinite set of bond paths radially directed from a nodal surface, a sphere $(1,+1)$ CPs.

The question of how one interprets the partitioning of a molecule that exhibits a ring attractor is readily accomplished by noting that the two-dimensional basin defined by the trajectories that terminate at the ring attractor serves as an interatomic surface for the two atoms whose nuclei serve as the termini of the associated cones of bond paths, the two Li atoms in Li_2^+, for example. The ring attractor is in effect an 'exploded' $(3,-1)$ bond critical point, which is itself a two-dimensional attractor whose 'basin' consists of the trajectories that terminate there and define the interatomic surface. The presence of a global attractor clearly partitions the 2S state of the hydrogen atom, the basin of the global attractor extending from the nodal surface to infinity, thereby violating Dalton's dictum that an atom be indivisible. The possibility of global attractors appearing upon electronic excitation in no way affects the usefulness or applicability of the topological theory of structure. If, for example, observed in highly excited Rydberg states of polyatomic molecules, a situation that has not so far been the case [5], they would enable one to treat the basin generated by the 'excited electron' as a separate entity with a definable set of contributing properties, prior to its separation from the system as a free electron.

Structurally, a global or ring attractor consists of a non-countable set of degenerate CPs, that is, CPs of rank less than three, and by virtue of the Palis-Smale theorem [18], they are structurally unstable. To quote Poston and Stewart [19], "Non-isolated critical points are especially nasty, but in a strong sense extremely uncommon…". Physically, an excited state where non-isolated CPs are found, has a brief and finite lifetime. Thus, unlike nuclear attractors, global and ring attractors are both physically and structurally unstable. The success of the atomic concept is doubtless a result of the dominance of isolated, point attractors in determining the structure of matter. However, whatever attractors are present, of rank one, two, or three, the classification afforded by the topological theory of structure and the resulting physical understanding will apply, as it is simply a reflection of the topology of the observable charge distribution, a distribution that, in turn, determines the observed physics.

The role of the zero-flux surface in quantum mechanics

While the zero-flux surface plays a central role in the topological theory of molecular structure, it was initially proposed as a spatial boundary because the mono-nuclear regions so defined recovered the chemistry of an atom in a molecule [20]. This natural definition satisfied the two essential requirements imposed on any possible definition of an atom in a molecule that stem from the concept of a functional group derived from experimental chemistry: it

maximized the transferability of the atom's distribution of charge from one system to another (the atom's form in real space) and this transferability in the density was accompanied by a paralleling transferability in the other properties of the atom including its energy. This finding is merely the satisfaction of the dictum that two atoms that look the same must necessarily make the same contributions to all properties. In particular, the kinetic energy density was found to parallel the transferability of the density, the observation that suggested the virial theorem should apply to such an atom in a molecule. An atomic statement of the virial theorem would lead to a unique partitioning of all properties, including its energy $E(\Omega)$, by allowing one to equate $E(\Omega)$ to $-T(\Omega)$ [20]. In 1975 this ''virial partitioning'', as postulated on the basis of the *observed* properties exhibited by molecular charge distributions, was shown to follow from Schrödinger's variation of his 'Hamilton integral' when extended to an open system by imposing the zero-flux surface, Eq. (1), as a boundary condition [21]. Shortly thereafter, it was realized [22] that this extension of Schrödinger's work was in reality an application of Schwinger's principle of stationary action [23] to a proper open system in a stationary state, one bounded by a surface of zero-flux, Eq. (1). Only somewhat later was the full topological significance of the zero-flux surface condition realized [7], leading eventually to a complete theory of molecular structure and structural stability [24].

The manner in which the zero flux surface condition, Eq. (1), is imposed as a boundary condition in the variation of either Hamilton's integral for a stationary state or of the action integral for a time dependent system is an important mathematical step in the theory. While introduced in 1975 [21], the most detailed statement of the imposition of this constraint is to be found in the thesis of Nguyen-Dang [24] with a somewhat condensed account being given in 1981 [25]. Because of its importance, the subject is worthy of further discussion and exemplification.

The zero-flux surface as a boundary condition

Every application of the variation principle to physics requires the imposition of boundary conditions and/or constraints. To obtain Schrödinger's 'wave equation' in the variation of what he termed the 'Hamilton integral', one imposes both the so-called natural boundary condition that $\nabla\psi \cdot \mathbf{n} = 0$ on the boundary at infinity and the constraint that the wave function be normalized, the Lagrange multiplier for the constraint being identified with the energy of the system [26]. To extend Schrödinger's variation principle to an open system one must necessarily add a further condition to be satisfied on the boundary of the open system.

For a one-electron system the natural boundary condition employed by Schrödinger, that $\nabla\psi \cdot \mathbf{n} = 0$, becomes identical with the zero-flux boundary condition for an open system, that $\nabla\rho \cdot \mathbf{n} = 0$ and Schrödinger's derivation then applies to both the total system and to an open system, if the latter is bounded by a surface of zero-flux. Wigner and Seitz used $\nabla\psi \cdot \mathbf{n} = 0$ and hence $\nabla\rho \cdot \mathbf{n} = 0$, as the boundary condition for obtaining solutions to Schrödinger's equation in their famous paper introducing the Wigner-Seitz cell in their study of solid sodium, considered as a one-electron system outside the core [27]. This was the first definition of an atom in a molecule. It is also the boundary condition used by Kohn in his derivation of a variational treatment of a one-electron model of a periodic lattice [28].

Before examining the manner in which the zero-flux boundary condition is imposed in the variation of the action integral in Schwinger's principle, we first give a word description of the process. Schwinger's principle is beautiful in its conceptual simplicity. It is a marriage of the principle of least action and Dirac's transformation theory. The action, denoted by $\hat{\mathbf{W}}_{12}$, connects two states of a system at the times t_1 and t_2. For a classical or a quantum system, it is the time integral of the Lagrangian which, in turn, is the spatial integral of a Lagrange energy density. Thus, the action integral incorporates the space-time volume generated by the system's temporal evolution. The principle of least action enables one to obtain the equation of motion by requiring that the action integral be stationary (a minimum) with respect to first-order variations in the path connecting two classical states at the times t_1 and t_2 or to variations of the state vector over the space-time volume bounded by the two quantum states at the two time limits. In the 'classical' principle of least action, also called Hamilton's extended principle, the boundary of the system is assumed to lie at infinity and the variations are set to zero at the two time end points. In addition, the variations in the state vector are also required to vanish on the spatial boundaries of the system. This restricted variation of the action integral yields the corresponding equation of motion, either Lagrange's equations or Schrödinger's equation, as the Euler equation when the variation of the action integral is required to vanish, that is when $\delta\hat{\mathbf{W}}_{12} = 0$.

Schwinger realized that by relaxing the condition that the variations vanish at the time end points and by varying the time itself at these end points he could, to use his own words, 'recover all of physics' for the total system from the variation of the action integral, and not just the equation of motion. This is accomplished by identifying the end point variations with the generators of infinitesimal canonical transformations in a classical system and infinitesimal unitary transformations in a quantum system. Such transformations can be used to describe all possible changes in any system, both temporal and spatial. It was Dirac who pointed out that such infinitesimal transformations lie at the heart of the correspondence between classical and quantum mechanics, noting that the temporal variation of an observable in quantum mechanics corresponded to 'the continuous unfolding of a unitary transformation', while the change in the dynamic variables in a classical system are the result of a corresponding 'continuous unfolding of a contact transformation' [29]. Thus, in his principle of stationary action Schwinger postulates that the variation of the action integral does not vanish but instead equals the difference in the action of the generators of infinitesimal (ε) canonical transformations – contact transformations in classical mechanics and unitary

transformations in quantum mechanics – at the two time end points t_1 and t_2. Thus, for a total system with boundaries at infinity, Schwinger's principle is stated as

$$\delta\hat{W}_{12} = \hat{F}(t_2) - \hat{F}(t_1) \tag{2}$$

This result may be restated in terms of a variation of the Lagrange function operator to obtain an operational form of the principle, a variational statement of the Heisenberg equation of motion for the generator $\hat{G}$

$$\delta\hat{L}\left[\hat{\Psi}, t\right] = \varepsilon(i/\hbar)\langle\hat{\Psi}\left|\left[\hat{H}, \hat{G}\right]\right|\hat{\Psi}\rangle \tag{3}$$

where $\hat{F}$ of Eq. (2) has been equated to $\varepsilon(i/\hbar)\hat{G}$. It is to be understood that the variation in the Lagrangian is caused by the action of the generator $\hat{G}$ on the state vector.

Equation (2) implies the equation of motion, since it states that the variation in the action vanishes except for the contributions from the time end-points, implying therefore, that $\delta\hat{W}_{12} = 0$ over the space-time volume, as for the restricted variation, the one that yields the Euler equation. In the general case of a system with finite boundaries, the space-time volume is bounded by a time-like surface which consists of the spatial boundary of the system at each instant of time, in addition to the space-like surfaces at the two time end-points, each of which represents the system at the given times t_1 and t_2. Schwinger gives an expression for the generalized variation of the action integral that includes variations on and of both the time-like and the space-like surfaces. Thus, while he stated his principle, Eq. (2), only for a total system with boundaries at infinity and hence without contributions from generators acting on the time-like surfaces, his general expression enables one to apply his principle to a system with finite boundaries, that is, to an open system. In doing so, one discovers, as detailed below, that extending the variation to an open system with unspecified boundaries does not yield the correct physics. Schrödinger's equation, already obtained from the variation of the action over the closed space-time volume, enables one to obtain an expression for the time rate-of-change of an expectation value for any open system, one that differs from the corresponding expression obtained from Schwinger's principle for arbitrary boundaries. To recover the correct physics for an open system from the *variational* principle of least action, one must impose the zero-flux surface constraint as a boundary condition on the time-like surface. The resulting open systems are termed proper open systems [1, 30].

surface when subjected to a variation $\delta\Psi$ of the state vector Ψ [25]. A region $\Omega(\Phi,t)$ is defined in terms of a 'well-behaved' trial function $\Phi = \Psi + \delta\Psi$, that is bounded by a zero-flux surface in $\nabla\rho_\Phi(\mathbf{r})$

$$\nabla\rho_\Phi(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \qquad \forall\ \mathbf{r}\ \in S(\Omega,\mathbf{r}_s) \tag{4}$$

where ρ_Φ is the density defined in terms of the trial function Φ. It is assumed that as Φ tends to Ψ at any time t, $\Omega(\Phi,t)$ is continuously deformable into the region $\Omega(t) = \Omega(\Psi,t)$ associated with the atom. The region $\Omega(\Phi,t)$ thus represents the atom in the varied total system, which is described by the trial function, just as $\Omega(t)$ represents the atom when the total system is described by Ψ. Imposing these conditions amounts to imposing the variational constraint that the divergence of $\nabla\rho_\Phi(\mathbf{r})$ integrates to zero at all stages of the variation which, in turn, implies the variational constraint that

$$\delta I[\Omega]_\Psi = \delta\left\{\int_{\Omega(t)} \nabla^2\,\rho(\mathbf{r},t)\,d\tau\right\} = 0 \tag{5}$$

It is important to understand that the zero-flux boundary condition, assumed to be maintained during the variation and denoted by δ is unidirectional in the sense that it implies

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n} = 0, \quad \forall\ \mathbf{r} \in S(\mathbf{r}_s) \Rightarrow \delta\int_\Omega d\tau\nabla^2\rho(\mathbf{r}) = 0 \tag{6}$$

but not the converse. The converse would demand only that the *integral* of flux in $\nabla\rho \cdot \mathbf{n}$ over the bounding surface of Ω be zero, and not that $\nabla\rho \cdot \mathbf{n} = 0$ locally, a condition that is neither made nor required for the variational derivation of the principle of stationary action.

It is possible [30] to express the variation of the action-integral operator or, more simply, of the Lagrange function operator for an open system with finite boundaries in a form that shows that it differs from that obtained for the total system, as given in Eq. (3), by a constant times the variation of the constraint integral $I[\Omega]_\Psi$, the form given in Eq. (7).

$$\delta\hat{L}\left[\hat{\Psi},t,\Omega\right] = (\varepsilon/2)\left\{(i/\hbar)\langle\hat{\Psi}\left|\left[\hat{H},\hat{G}\right]\right|\hat{\Psi}\rangle_\Omega + \text{complexconjugate}\right\} - \left(\hbar^2/4m\right)\delta I_\Psi \tag{7}$$

Clearly, the variational constraint given in Eq. (5), that arises from imposing the zero-flux boundary condition, Eq. (4), at every stage of the variation, causes the expression for the variation of the Lagrange function operator given in Eq. (7), to reduce to the result given in Eq. (8):

$$\delta\hat{L}\left[\hat{\Psi},t,\Omega\right] = (\varepsilon/2)\left\{(i/\hbar)\langle\hat{\Psi}\left|\left[\hat{H},\hat{G}\right]\right|\hat{\Psi}\rangle_\Omega + \text{complex conjugate}\right\} \tag{8}$$

The critical step in the imposition of the zero-flux boundary condition concerns the continuous deformability assumed for a region bounded by a zero-flux a statement of the principle of least action that is a generalization of Schwinger's expression for a total system, Eq. (3). Open systems described by Eq. (8) are

termed 'proper open systems.' Eq. (8) applies to any region of space bounded by a zero-flux surface, the total system and its constituent proper open systems. It is a variational statement of the Heisenberg equation of motion for the generator (observable) $\hat{G}$ and is the operational statement of Schwinger's principle. A single principle that, as claimed by Schwinger, recovers "all of physics", a description that includes as well, the physics of an open system. As well as yielding Schrodinger's equation of motion, one also obtains the commutation relations through the action of the generator $\left(\partial\hat{L}/\partial(\mathrm{d}\hat{q}_r/\mathrm{d}t)\right)\delta\hat{q}_r$ on the coordinate and conjugate momentum operators.

As noted above, the variation without the imposition of the zero-flux boundary condition does not recover the physics of an open system, as required by Schrödinger's equation. Thus, one finds that the contribution from the variations associated with the boundary of an open system with arbitrary boundaries is given by [31]:

$$\oint \mathrm{d}\mathbf{S}(\mathbf{r}_\mathrm{a}) \cdot \left(-\hbar^2/2m\right)\left(\nabla\hat{\Psi}^{+}\delta\hat{\Psi}+\mathrm{c.c.}+\mathbf{n}\hat{L}\delta\mathbf{S}(\mathbf{r}_\mathrm{s})\right) \tag{9}$$

where $\hat{L}$ is the Lagrangian density and $\mathrm{S}(\mathbf{r}_\mathrm{s})$ denotes the variation of the boundary. The corresponding term appears in the variation of the boundary of Schrödinger's variation of his energy functional for a system in a stationary state. The imposition of the constraint given in Eq. (5) rids the variational expression of the unoperational surface variation $\delta\mathrm{S}(\mathbf{r}_\mathrm{s})$ to yield the required physical result presented in Eq. (10):

$$(\varepsilon/2)\oint \mathrm{d}\mathbf{S}(\mathbf{r}_\mathrm{s}) \cdot (\mathbf{J}_\mathrm{G}(\mathbf{r})+\mathrm{c.c.}) \tag{10}$$

where $\mathbf{J}_\mathrm{G}(\mathbf{r})$ is the current density for the generator $\hat{G}$ [31]. The surface flux in the current density of the generator as given in Eq. (10) is essential to the description of the properties of an open system.

From boundary variations to generators of physical change

The purpose of generalizing the variation of the action integral to include the variations on and of the time-like and space-like surfaces is to complete the physical description of a system through the identification of the boundary variations with the generators of infinitesimal unitary transformations; the identification $\delta\Psi = -\varepsilon(\mathrm{i}/\hbar)\hat{G}\Psi$. Thus, to apply the physical variations envisaged in the principle of stationary action to either the total system or one of its open systems, *one assumes the existence of a special class of trial functions* Φ; a class of functions that when subjected to variations corresponding to real physical changes in the system will necessarily exhibit the property of continuous deformability of a region $\Omega(\Phi,\mathrm{t})$ into the region $\Omega(\Psi,\mathrm{t})$.

One readily demonstrates instances where this hypothesis is clearly verified for the coordinate changes that result from the action of a number of important elementary infinitesimal unitary transformations. The action of the generator of an infinitesimal unitary transformation can be represented by the operator $\hat{U}$ and its inverse $\hat{U}^{-1}$ which equals the Hermitian adjoint,

$$\hat{U} = \hat{I} - (\mathrm{i}\varepsilon/\hbar)\hat{G} = \mathrm{e}^{-(\mathrm{i}\varepsilon/\hbar)\hat{G}} \quad \hat{U}^{-1} = \hat{I}+(\mathrm{i}\varepsilon/\hbar)\hat{G} = \mathrm{e}^{+(\mathrm{i}\varepsilon/\hbar)\hat{G}} \tag{11}$$

and $\hat{U}\hat{U}^{-1} = \hat{I}$ to order ε^2, where $\hat{I}$ denotes the unit operator. The action of the transformation on an observable $\hat{A}$ is described by

$$\delta\hat{A} = \hat{A} - \hat{A}' = \hat{A} - \hat{U}\hat{A}\hat{U}^{-1} = (\mathrm{i}\varepsilon/\hbar)\left[\hat{G},\hat{A}\right] \tag{12}$$

and the change induced in the state vector is given by $\delta\Psi = -\varepsilon(\mathrm{i}/\hbar)\hat{G}\Psi$. One notes that the corresponding change caused by an infinitesimal canonical transformation – a contact transformation – of a property A in classical mechanics is given in terms of the Poisson bracket as $\delta\mathrm{A} = \varepsilon[\mathrm{A},\mathrm{G}]_\mathrm{P}$, We consider, in turn, a number of elementary transformations, each of which when employed in Eq. (8) yields a corresponding theorem for a proper open system – for an atom in a molecule.

1. Setting $\hat{G} = \mathbf{p}$ as the generator in Eq. (8), yields the atomic statement of the Ehrenfest force theorem, the time derivative of the electronic momentum. This transformation, by Eq. (12) with $\hat{A} = \mathbf{r}$, induces an infinitesimal uniform translation of the electronic coordinate $\mathbf{r}$ by $-\boldsymbol{\varepsilon}$ and thus $\mathbf{r}' = \mathbf{r}-\boldsymbol{\varepsilon}$. Clearly, such a transformation at any stage of the variation process, simply translates a zero-flux surface by the amount $-\boldsymbol{\varepsilon}$ and the requirement of the continuous deformability of a region $\Omega(\Phi,\mathrm{t})$ into the region $\Omega(\Psi,\mathrm{t})$ is maintained throughout. The Ehrenfest force is the force that is measured in the operation of an atomic force microscope [31].
2. Setting $\hat{G} = \mathbf{r}\cdot\mathbf{p}$ as the generator in Eq. (8), yields the atomic statement of the virial theorem, the theorem that enables one to define the electronic energy of an open system and the pressure acting on it [32]. The effect of this transformation is to induce a scaling of the electronic coordinate $\mathbf{r}$ by the factor $\zeta = \mathrm{e}^{\varepsilon}$ and the effect of $\hat{U}(\varepsilon)$ on the state vector yields a properly normalized function with the coordinate $\mathbf{r}$ scaled by ζ. If $\rho'(\mathbf{r})$ denotes the transformed density viewed as a function of $\mathbf{r}$, then $\nabla\rho'(\mathbf{r}) = \zeta\nabla'\rho(\mathbf{r}')$ and the zero-flux surface is transformed into another surface of zero-flux.
3. Setting $\hat{G} = \mathbf{r}$ as the generator in Eq. (8), yields the atomic current theorem, since the time derivative of an electronic coordinate is an electronic velocity, or electronic current. It is this theorem that, among other things, makes possible the partitioning of the magnetic susceptibility into atomic contributions [33]. The effect of this generator is to transform $\mathbf{r}$ into itself and the effect of $\hat{U}(\mathbf{r})$ on the state vector is to induce a phase transformation. Thus the density and its properties are left unchanged by this transformation and the property of zero-flux is maintained throughout the variation.
4. Setting $\hat{G} = \mathrm{N}\hat{I}$, the number operator whose expectation value determines an atomic population [34], yields the integrated equation of continuity when

used as the generator in Eq. (8). It clearly leaves the state vector and the density unchanged when used as the generator.

5. Setting $\hat{G} = \hat{H}$ and $\varepsilon = dt$ yields the temporal generator $-(i/\hbar)\hat{H}\,\delta t$, the generator that describes the 'continuous unfolding' of the state vector and of all properties, including the density. The continuous evolution of the density as a function of time ensures a corresponding continuous development of the zero-flux surface.

These examples of generators, which yield the most important of the atomic theorems that determine the mechanics of an open system [35], all induce infinitesimal unitary transformations that meet the requirement of causing a continuous deformation of a region $\Omega(\Phi,t)$ into the region $\Omega(\Psi,t)$. Could one construct a trial function that satisfied the necessary boundary conditions at infinity, including the vanishing of $\delta\Phi$ when employed in the variation of the action integral, but did not yield a continuous mapping of a region $\Omega(\Phi,t)$ bounded by a zero-flux surface into a similarly bounded region $\Omega(\Psi,t)$? Perhaps, but then such a discontinuous transformation would not correspond to the action of a generator of an infinitesimal coordinate transformation as required by Schwinger's identification of the mathematical variation in the state vector with the generator of an infinitesimal unitary transformation, that is, the identification $\delta\Psi = -\varepsilon(i/\hbar)\hat{G}\Psi$, where $\hat{G}$ *is a physical observable*. The principle of stationary action is after all, not a mathematical theorem, but a statement of a physical principle.

Conclusions

The application of the defining equation of a zero flux surface, Eq. (1), to a charge distribution whose topology exhibits only isolated point attractors, leads to the disjoint and exhaustive partitioning of space into a set of regions, each of which contains a single nucleus. This statement is contingent upon the use of the Coulombic Hamiltonian in the description of the system of interest, an acceptable procedure for energies up to those required for plasma formation. The topological definition of structure and the accompanying physical understanding it affords survive the presence of non-isolated attractors found in excited states of one-electron systems. The topology of the electron density is a consequence of and summarizes that physics that underlies the form of matter. Whatever new topological features the charge density may be found to exhibit, as a consequence of its averaging over nuclear motions for example, they may be incorporated into an expanded theory to provide a still deeper understanding of the behavior of matter.

The core of Schwinger's principle of stationary action is the introduction of the variation of the state vector on the space-time boundary defined by the temporal evolution of a system and the variation of the boundary itself in conjunction with the subsequent identification of these variations with the generators of infinitesimal unitary transformations. Thus, the theory requires the use of a special class of trial functions: those whose variation will correspond to continuous changes in the coordinates of the physical system, the very requirement needed to ensure the applicability of the zero-flux surface condition as the defining constraint of an open system.

Acknowleedgements The author wishes to thank Professor Nguyen-Dang for useful comments concerning this manuscript.

References

1. Bader RFW (1990) Atoms in molecules: a quantum theory. Oxford University Press, Oxford, UK
2. Spackman MA (1998) Royal Soc Chem: Ann Rep Section C 94: 183
3. Bader RFW (998) J Phys Chem A 102: 7314
4. Bader RFW (1998) Can J Chem 76: 973
5. Bader RFW, Bayles D, Heard GL (2000) J Chem Phys 112: 10095
6. Bader RFW, Runtz GR (1975) Mol Phys 30: 117
7. Bader RFW, Anderson SG, Duke AJ (1979) J Am Chem Soc 101: 1389
8. Kato WA (1957) Commun Pure Appl Math 10: 151
9. Steiner E (1963) J Chem Phys 39: 2365
10. Wheeler JA (1949) Rev Mod Phys 21: 133
11. Elton LBR (1950) Proc Roy Soc (London) A 63: 1115
12. Greiner W (1981) Theoretische Physik: Relativistic Quantum Mechanics. Verlag Harri Deutsch, Notes: p 353
13. Zou PF, Bader RFW (1994) Acta Cryst A 50: 714
14. Pendás AM, Costales A, Luaña Y (1997) Phys Rev B 55: 4275
15. Bader RFW, Platts JA (1997) J Chem Phys 107: 8545
16. Bader RFW, Nguyen-Dang TT, Tal Y (1981) Rep Prog Phys 44: 893
17. Bader RFW, Johnson S, Tang T-H, Popelier PLA (1996) J Phys Chem A 100: 15398
18. Palis J, Smale S (1970) Pure Math 14: 223
19. Poston T, Stewart I (1978) Catastrophe Theory and its Applications. Pitman, London
20. Bader RFW, Beddall PM (1972) J Chem Phys 56: 3320
21. Srebrenik S, Bader RFW (1975) J Chem Phys 63: 3945
22. Bader RFW, Srebrenik S, Nguyen Dang TT (1978) J Chem Phys 68: 3680
23. Schwinger J (1951) Phys Rev 82: 914
24. Nguyen-Dang TT (1980) PhD Thesis, McMaster University, Hamilton, Ontario, Canada, p 98
25. Bader RFW, Nguyen-Dang TT (1981) Ad Quantum Chem 14: 63
26. Schrödinger E (1926) Ann D Phys 79: 361
27. Wigner E, Seitz F (1933) Phys Rev 43: 804
28. Kohn W (1952) Phys Rev 87: 472
29. Dirac PAM (1958) The Principles of Quantum Mechanics. Oxford University Press, Oxford, UK
30. Bader RFW (1994) Phys Rev B 49: 13348
31. Bader RFW (2000) Phys Rev B 61: 7795
32. Bader RFW, Austen MA (1997) J Chem Phys 107: 4271
33. Bader RFW, Keith TA (1993) J Chem Phys 99: 3683
34. Bader RFW, Zou PF (1992) Chem Phys Lett 191: 54
35. Bader RFW, Popelier PLA (1993) Int J Quantum Chem 45: 189